# METHODS FOR THE PRODUCTION OF CRYSTALLIZED GLASS PANEL WITH EMBOSSED SURFACE

## FIELD OF INVENTION

[0011] This invention relates to the process of producing flat crystallized glass panel with embossed surface which results stereoscopic aspect and better static friction on the surface to prevent from slipping under wet condition, so it can better be used on floor application and others.

## BACKGROUND OF THE INVENTION

[0021] The crystallized glass is an ideal substitution of natural stone as ornamental building materials because of its superior mechanical strength, heat resistance, and efflorescence resistance. Conventional crystallized glass articles have glossy and smooth surface, and therefore have very limited application on floor due to the potential risk of slip.

[0022] Manufacture of crystallized glass articles begins with production of a crystallizable glass composition by heating the special formulated, mixed raw materials of glass at a temperature of over 1400° C. Granules of crystallizable glass are typically packed into a mold for crystallization. Upon completion of the crystallization, the integral crystallized glass article is obtained .

[0023] The-six general steps of manufacturing crystallized glass articles are:

[0024] (1) Crystallizable glass is formulated such as from the systems $SiO_2$-$Al_2O_3$-CaO, $SiO_2$-$Al_2O_3$-CaO-ZnO, or others may be employed. The formulated glass materials are heated at 1400 to 1600° C. to melt them together.

[0025] (2) Water granulation: The molten crystallizable glass of step 1 is granulated in water into glass particles with less than 10 mm in size. The ideal water temperature is

around 40 to 60° C. The crystallizable glass granules are collected and dried.

[0026] (3) Molding: The crystallizable glass granules are packed into a flat refractory mold with surrounding frames. The floor of the mold and interior surfaces of the frames are coated with a mold release agent such as alumina powder.

[0027] (4) Crystallizing: The loaded mold is heat treated using a specified temperature profile, such that the glass granules are softened, deformed and fusion-bonded together along their interfaces. Needle-like crystals are formed from the surface of the glass granules toward the interior (crystallization).Conventionally, the loaded mold is heated at a constant rate and may be held at a high temperature for as much as one to two hours. In completion of the crystallizing process, the integral crystallized glass article is obtained.

[0029] (5) Cooling: A proper temperature profile is applied for cooling, so the glass article will not crack or distort.

DISCUSSION OF PRIOR ART

[0012] Crystallized glass has been utilized in the manufacturing of such varied articles as cookware, tableware, missile nose cones, protective shields, and in the computer and electronics field. Nowadays, crystallized glass has been used as ornamental building materials to replace the natural stones due to its excellent characteristics in mechanical strength, heat-resistance, chemical corrosion strength, and water resistance, and has obtained great popularity. However, its glossy and smooth surface together with its pure color often creates simple and cold environmental feelings. Several patents (G.B. 1427792, 1972; U.S. Pat. No. 3,843,343, 1974, Okada et al.; U.S. Pat. No. 3,955,989, 1976, Nakamura; U.S. Pat. No. 5,403,664, 1995, Kurahashi et al.) disclose the methods of producing surface pattern over crystallized glass flat panel. However, these methods are limited in changing the color pattern of the surface rather than the roughness of the surface. As a result, the crystallized glass has inherited the smooth and glossy characteristic of glass and has limited its use from floor application due to the potential

risk of slip.

[0013] The U.S. Pat. No. 5,089,345, 1992, Hashibe et al. states that it is uneconomical to apply molds with rough and uneven surface to produce crystallized glass with uneven surface, and discloses a method of producing crystallized glass with an irregular rough surface pattern. However, the rough surface is produced by overlapping flaky and flattened crystallized pieces at "random" at the bottom of the glass article. The resulted surface is therefore unpredictable.

[0014] Many U.S. Patents (U.S. Pat. No. 3,554,725, 1971, Bracken et al.; U.S. Pat. No. 3,672,859, 1972, Classen; U.S. Pat. No. 4,746,347, 1988, Sensi; U.S. Pat. No. 5,885,315, 1999, Fredholm et al.) disclose methods of using molten glass to form glass sheets with rough surface patterns through mechanical rollers. However, the process is not adequate for producing crystallized glass suitable for use in flooring.

Crystallized glass, also known as glass ceramic, could be a desirable material for flooring. Glass ceramic is beautiful and durable.

Floors of polished stone or conventional glass ceramic have two disadvantages. The reflective surface can be unattractive or painful to the eyes under certain lighting. The surface is slick and can be dangerous to walk on, especially if any oil or moisture are present.

There is thus a need for glass ceramic flooring that does not reflect light in a mirror-like manner. There is further a need for glass ceramic flooring that has a higher coefficient of friction than polished stone or conventional glass ceramic, so that the flooring is safe to walk on even when wet.

SUMMARY OF INVENTION

[0032] The present invention provides two related methods in producing crystallized glass plates with an embossed, that is, textured, surface. Both methods result in a textured

top surface of the glass ceramic plate after the flow deformation this sense step. The texturing of the finished plate is ornamental; but more importantly, it greatly reduces glare and slipperiness of the plate, even when wet. Crystallized glass plates produced by the methods of the present invention have a coefficient of friction that is at least 20% greater than that of crystallized glass plates produced by conventional methods. The methods of the present invention require no special equipment or molds and are easily adapted for mass production of glass ceramic articles of consistent quality.

[0033] Method 1 relies solely on careful control of the temperature profile during the flow deformation step to produce a glass ceramic plate with a suitably textured top surface that is free of pinholes. After polishing, the finished plate has a surface that is textured by a network of unpolished craters that are about 0.2 to 0.5 mm deep.

[0034] Method 2 further includes loading the mold with flat pieces of crystallized glass underneath the granules of crystallizable glass. The finished plate has a surface that is textured by raised areas above the flat pieces of precrystallized glass. The raised areas are typically about half as high as the original thickness of the precrystallized glass.

BRIEF DESCRIPTION OF DRAWINGS

[0035] FIG 1a illustrates that the glass body is prepared by loading various sizes of glass particles into the mold and ready for crystallization process.

[0036] FIG 1b (Prior Art) illustrates a smooth top surface created by the flow deformation process if the crystallizing step is performed at high temperature or for long period of time.

[0037] FIG 1c illustrates that to control the flow deformation using method 1 of the present invention creates a non-smoothed surface.

[0038] FIGS. 2a & 2b are diagrams that illustrate the thickness of glass body before and after the crystallization process.

[0039] FIGS. 2c & 2d are diagrams that illustrate the thickness of glass body, before and after crystallization process, which mixes the glass bits with flat glass pieces together.

[0040] FIG. 2e illustrates the method of loading the glass particles with both glass bits and glass pieces.

[0041] FIG. 2f illustrates the result of the crystallized glass panel with an uneven surface of 2e.

DETAILED DSCRIPTION

[0042] Method 1: The present invention to control the flow deformation process, so the spaces among glass particles are filled with glass flow, but the glass particles are not completely flattened down. To do so, we divide the procedure into two steps as follows:

[0043] 1) keep the glass body at a temperature lower than the temperature that the flow deformation process needs (about 20° C. below liquidus temperature) for a period of time, then

[0044] 2) raise up the temperature to where the flow deformation process requires for time as needed.

[0045] The first step of process provides enough time for the crystals to grow within the glass body. It also prepares the glass body in temperature close to the flow deformation process needs, so the flow can happen quickly as soon as the temperature rises. In step two, we control the time factor of the process to obtain the desired surface condition as we needed. It is important to know that the formula of glass, the size of the glass particles, the type of furnace used, and the required deviation in depth over the surface are all important factors in determining those temperature and time parameters. The basic procedure is as follows:

[0046] 1. To prepare crystallizable glass bits with size of 10 mm or less such as by water granulation.

[0047] 2. Apply mold release agent, such as alumina powder, over the refractory mold and frames to prevent the glass from adhering on the mold during the crystallization.

[0048] 3. Putting the glass bits created in step 1 into the mold over the mold release agent and leveling the surface.

[0049] 4. Place the mold into furnace for crystallization heat-treatment.

[0050] 5. Maintain the glass body about 20° C. below the liquidus temperature for approximately 40 minutes, so the crystals are formed inside the glass bits and the glass bits are all fusion-bonded together

[0051] 6. Kept the glass body at the temperature where the flow deformation process requires for a period of time such that spaces among glass particles are filled with glass flow, but the glass particles are not completely flattened down.

[0052] 7. Polishing the surface to remove sharp bumps such that a textured surface with craters with a depth of 0.2 to 0.5 mm is produced.

[0053] Method 2: The thickness of the crystallized glass article is usually about 40% 60% (depends upon the size of particles) of the height of the glass body before it is crystallized, This is due to the fact that different size of glass particles, after fusion bonded together, produces different porous body, and therefore results different density of the article (ref U.S. Pat. No. 4,054,435). On the other hand, the density of the glass body varies the thickness of the glass article. It is our invention to load the glass body with different glass particles, so it has different density in different locations among the glass body. Controlling the time of flow deformation process can produce crystallized glass panel with un-even surface. The basic procedure is as follows:

[0054] 1. To prepare crystallizable glass bits with size of 5 mm or less such as by water granulation.

[0055] 2. To prepare flat crystallized glass pieces with thickness and shapes desired (circle, square, etc.).

[0056] 3. Apply mold release agent over the refractory mold and frames to prevent the glass from adhering on the mold during the crystallization.

[0057] 4. Place the flat crystallized glass pieces prepared in step 2 on the mold over the mold release agent in position desired.

[0058] 5. Fill up the mold with glass bits prepared in step 1. The glass bits typically cover the surface of the flat crystallized glass pieces.

[0059] 6. Place the mold into furnace for crystallization heat-treatment.

[0060] 7. Maintain the glass body about 20° C. below the liquidus temperature for approximately 40 minutes, so the crystals are formed inside the glass bits and the glass bits are all fusion-bonded together

[0061] 8. Kept the glass body at the temperature where the flow deformation process requires for a period of time or such that. spaces among glass particles are filled with glass flow, but the glass particles are not completely flattened down.

[0062] 9. Polishing the surface such that a textured surface with raised areas up to 1.2 mm in height is produced.

EXAMPLES

[0063] The crystallizable glass bits used in preparing the examples are compositions of the $SiO_2$-$Al_2O_3$-CaO-ZnO system. The size of the mold is around 1000 mm.times.1000 mm. The refractory mold is coated with alumina to prevent the glass from adhering on the mold during the crystallization.

Example 1

[0064] Two sizes of crystallizable glass bits are used, one with size between 3-5 mm (type A) and another with size 3 mm or less (type B). Load 25 kg glass bits of type B into the mold over the mold release agent and level the surface. Load another 25 kg glass bits of type A into mold over the glass bits previously loaded. Leveling the surface. Place the mold into furnace, bring temperature to 1115.degree. C. and maintain temperature for 40 minutes. The crystals are then formed inside the glass bits and the glass bits are all fusion-bonded together. Increase the temperature to 1135° C. and maintain temperature for 30 minutes. In completion of cooling process, polish the surface as desired. The polished article has craters on surface uniformly with average size >5 mm and depth of 0.2 0.5 mm.

Example 2

[0065] The crystallizable glass bits with size of 3 mm or less and flat crystallized glass pieces with size of 30 mm.times.30 mm and thickness of 3 mm are used. The flat crystallized glass pieces are placed on the mold over the mold release agent with 100 mm apart. Load 50 kg glass bits into the mold over flat glass pieces and level the surface. Place the mold into furnace and follow its regular temperature profile for heat-treatment. Maintain the temperature to 1115.degree. C. for 40 minutes. The crystals are then formed inside the glass bits and the glass bits are all fusion-bonded together. Maintain the temperature to 1135.degree. C. for 30 minutes. In completion of cooling process, polish the surface as desired. The polished article has square shaped bumps on surface uniformly with average size <30 mm and depth <1.2 mm.